Trace Elements in Soils and Plants

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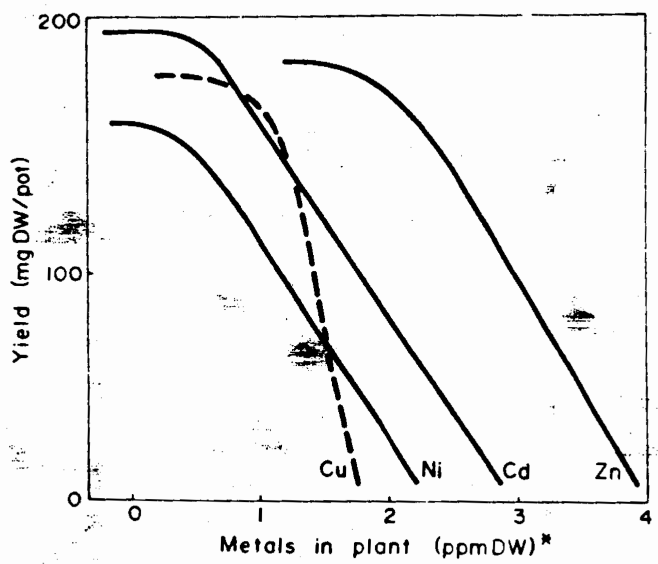

FIGURE 2. Response of young barley plants to heavy metal concentrations in their tissues. Asterisk indicates concentration of metals is given in powers of ten.[59]

A review of the literature does not reveal any generally adequate method for rapid reclamation of soils heavily contaminated by trace metals. The effects of each treatment will depend upon soil properties, mainly on CEC and on plant response. Therefore, the reclamation or improvement of arable land polluted with trace elements needs to be designed for a specific plant-soil system.

V. PLANTS

The significant role of plants in both cycling of trace elements and contaminating the food chain has been well illustrated for various ecosystems and published in numerous papers. Plants can accumulate trace elements, especially heavy metals, in or on their tissues due to their great ability to adapt to variable chemical properties of the environment, thus plants are intermediate reservoirs through which trace elements from soils, and partly from waters and air, move to man and animals. As Tiffin[789] has concluded, plants may be passive receptors of trace elements (fallout interception or root adsorption), but they also exert control over uptake or rejection of some elements by appropriate physiological reactions.

One of the basic environmental problems relates to the quantities of accumulated metals in plant parts used as food. Special attention also should be given to the forms of metals distributed within plant tissues, for the metal forms in plants seem to have a decisive role in metal transfer to other organisms.

Several authors have observed that the yield of various crops can be decreased due to metallic pollution (Figure 2). The generalized effects of metal concentrations in nutrient solution on yield and metal content of plants are shown in Figure 3. Most important, however, are the biological and health effects on man and animals caused by metallic pollution in plants. This subject has been reviewed in detail by many textbooks on environmental health.

Each case of plant pollution is unique and should be studied for a specific environment. There is an increasing awareness that results of studies based on simulation-type systems cannot be related to those in a natural system. This fact is supported by de Vries and Tiller,[831] who reported a much lower absorption of heavy metals by lettuce and onions grown in a market garden soil than by those grown under greenhouse and miniplot conditions.

8. Soil characteristics, e.g., pH, free carbonates, organic matter, clay content, and moisture
9. Input-output balance
10. Plant sensitivity

Lewin and Beckett[469] widely reviewed monitoring of heavy metal accumulation in agricultural soils treated with sewage sludge and pointed out that it will be unreasonable to assume, without checks, whether heavy metals in soil will become immobilized with time or not.

Different soil types, plant species, and growing conditions contribute to the divergent influences of soil contamination on trace element status in plants. Some authors use a term "soil resistance to heavy metal contamination", which is related to the critical levels of metallic pollutants that exhibit toxic effects on plants and environments. This term is largely related to the cation exchange capacity (CEC) of soils (see Chapter 3, Section III.D.). Usually the resistance of a nonacid heavy soil with a higher content of organic matter exceeds several times the resistance of a light sandy acid soil. Loamy neutral soils may accumulate a higher amount of trace elements with much less environmental risk. However, a general chemical imbalance of such soils usually results in decreased biological activity, decreased or increased pH, and, as a further consequence, in degradation of organic and mineral sorption complexes.

Contamination of agricultural soils has already become relatively common and is likely to continue. Noticeable, also, is the fact that most often soils become contaminated by several metallic pollutants that are accompanied quite frequently by acid rains (mainly SO_2 and HF). Such an association of pollutants in soil greatly complicates their impact on the environment.

B. Soil Reclamation

The improvement of soils damaged and contaminated by pollutants has recently become a great practical problem. Reclamation of the particular soil requires, in so far as possible, a full understanding of soil properties and of the deteriorating factors. Soil contamination with heavy metals is usually quite permanent, as has been reported by Davies,[166] Johnson et al.,[365] Purves,[634] and Kitagishi and Yamane.[395] Therefore, it is necessary to emphasize that a soil heavily contaminated, especially by trace metals, is likely to be the sink of these contaminants, resulting in degradation of biological and chemical properties of the soil.

Several specific techniques for amelioration of various industrial wastes and for their revegetation have been described by Gemmell.[260] For soils contaminated by trace elements, the practices advised to prevent plant pollution are based on two main reactions — the leaching of easily soluble elements and the immobilization of microcations in soils. Heavily contaminated soil may need some special treatment, as was done by Kobayashi et al.[405] who removed an excess of soil Cd by repeated treatment with EDTA solution and lime (the Cd content of the surface soil decreased from 27.9 to 14.4 ppm). Mixing polluted topsoils with unpolluted soil material, as well as covering over the polluted soils, or replacement of the polluted topsoils, as reported by Kitagishi and Yamane[395] have been used for arable soils in Japan.

Reclamation of soils contaminated by heavy metals is usually based on the application of lime and phosphates and the addition of organic matter. The addition of lime, resulting in increased soil pH, however, does not always bring the expected results in the immobilization of some trace metals. The metals that are most likely to occur in soil as organic chelates in larger particulates may become soluble quite easily after heavy liming, as has been reported mainly for Cu, Zn, and Cr.[152,260,618] In most cases, however, lime and phosphate are quite effective in lowering heavy metal concentrations in plants, especially those growing on acid sandy soils. This response is an effect of both chemical and physical reactions in soil materials and cation interactions physiologically characteristic of a plant.

Table 6
TOTAL CONCENTRATIONS OF TRACE ELEMENTS CONSIDERED AS PHYTOTOXICALLY EXCESSIVE LEVELS IN SURFACE SOILS (PPM DW)

	Concentrations as given by various authors					
Element	**a**	**b**	**c**	**d**	**e**	**f**
Ag	—	—	2	—	—	—
As	—	50	25	30	20	15
B	30	100	—	100	25	—
Be	—	10	—	10	10	—
Br	—	—	—	20	10	—
Cd	—	5	8	5	3	—
Co	30	50	25	50	50	50
Cr	—	100	75	100	100	—
Cu	60	100	100	100	100	125
F	—	500	—	1000	200	—
Hg	—	5	0.3	5	2	—
Mn	3000	—	1500	—	—	—
Mo	4	10	2	10	5	—
Ni	—	100	100	100	100	100
Pb	—	100	200	100	100	400
Sb	—	—	—	10	5	—
Se	—	10	5	10	10	—
Sn	—	—	—	50	50	—
Tl	—	—	—	—	1	—
V	—	—	60	100	50	—
Zn	70	300	400	300	300	250

Note: Sources are the following: a, 419; b, 206; c, 479; d, 376a; e, 398; and f, 395.

et al.[59] concluded that in addition to the commonly monitored levels of Cu, Ni, Zn, Cd, Cr, and Pb during the disposal of sewage sludge on farm land, it may be necessary to monitor levels of Ag, Ba, Co, Sn, As, and Hg and also possibly Mo, Bi, Mn, and Sb, until their likely accumulations in surface soil can be shown to be harmless.

Soil contaminated with heavy metals can produce apparently normal crops that may be unsafe for human or animal consumption. Kloke[398] calculated that if the content of Hg, Cd, and Pb in the soil is not higher than the threshold values (Table 6), it can be expected that the contents of these metals in human diets will not exceed weekly tolerable intakes established by FAO/WHO.[398] Therefore, safe use of sewage sludge must be assessed on the basis of a safe addition of trace metals into soils.

Permissible levels of trace elements, particularly heavy metals, used on farmland can be calculated based on several factors. It is most important, however, to evaluate acceptable application rates in relation to:

1. Initial trace element content of soil
2. Total amount added of one element and of all heavy metals
3. Cumulative total load of heavy metals
4. Heavy metal dose limitation
5. Equivalency of trace element toxicity to plants
6. Threshold values of trace element concentrations in soils
7. Relative ratios between interacting elements

Table 5
AGRICULTURAL SOURCES OF TRACE ELEMENT CONTAMINATION IN SOILS (PPM DW)

Element	Sewage sludges[a]	Phosphate fertilizers[b]	Limestones[c]	Nitrogen fertilizers[d,l]	Manure[c]	Pesticides[e] (%)
As	2—26	2—1,200	0.1—24.0	2.2—120	3—25	22—60
B	15—1,000	5—115	10	—	0.3—0.6	—
Ba	150—4,000	200	120—250	—	270	—
Be	4—13	—	1	—	—	—
Br	20—165	3—5	—	185—716[f]	16—41	20—85
Cd	2—1,500	0.1—170	0.04—0.1	0.05—8.5	0.3—0.8	—
Ce	20	20	12	—	—	—
Co	2—260	1—12[g]	0.4—3.0	5.4—12	0.3—24[g]	—
Cr	20—40,600	66—245	10—15	3.2—19	5.2—55	—
Cu	50—3,300	1—300	2—125	<1—15	2—60	12—50
F	2—740	8,500—38,000[h]	300	—	7	18—45
Ge	1—10	—	0.2	—	19	—
Hg	0.1—55	0.01—1.2[d]	0.05	0.3—2.9	0.09—0.2	0.8—42
In	—	—	—	—	1.4	—
Mn	60—3,900	40—2,000	40—1,200	—	30—550	—
Mo	1—40	0.1—60	0.1—15	1—7	0.05—3	—
Ni	16—5,300	7—38[d]	10—20	7—34	7.8—30	—
Pb	50—3,000	7—225[i]	20—1,250	2—27	6.6—15	60
Rb	4—95	5	3	—	0.06	—
Sc	0.5—7	7—36	1	—	5	—
Se	2—9	0.5—25[j]	0.08—0.1	—	2.4	—
Sn	40—700	3—19[d]	0.5—4.0	1.4—16.0	3.8	—
Sr	40—360	25—500	610	—	80	—
Te	—	20—23	—	—	0.2	—
U	—	30—300[k]	—	—	—	—
V	20—400	2—1,600[d]	20	—	—	45
Zn	700—49,000	50—1,450	10—450	1—42	15—250	1.3—25
Zr	5—90	50	20	—	5.5	—

[a] Refs. 70, 249, 593.
[b] Refs. 94, 381, 399.
[c] Refs. 20, 25, 249, 532.
[d] Ref. 701.
[e] Ref. 510.
[f] Ref. 875
[g] Ref. 744.
[h] Refs. 55, 620.
[i] Ref. 755a.
[j] Ref. 809.
[k] Ref. 306.
[l] Mainly ammonium sulfate.

orchards or in other locations by contamination from industrial emissions or heavy and repeated applications of sewage sludges. A high heavy metal content of sludges is the most important hindrance to their use in agriculture. Although Purves[634] reported that in practice the concern with using sludges commonly is only their phytotoxicity due to excesses of Zn, Cu, and Ni, their content of Cd in particular, as well as of Pb and Hg, should be of concern as serious health risks. As Andersson and Nilsson[25] have observed, long-term use of sewage sludge increased the soil levels of Zn, Cu, Ni, Cr, Pb, Cd, and Hg. Of these elements, however, only Zn, Cu, Ni, and Cd were increased in cereal grains, and Zn, Cu, Cr, and Pb were increased in cereal straw. Chaney[127] and Sikora et al.[726] recommended higher doses of sewage sludges because of the relatively low availability of heavy metals to plants. Beckett

IV. SOIL

A. Soil Contamination

Soil is a very specific component of the biosphere because it is not only a geochemical sink for contaminants, but also acts as a natural buffer controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota. Trace elements originating from various sources may finally reach the surface soil, and their further fate depends on soil chemical and physical properties. Although the chemistry of soil contaminants recently has been the subject of many studies, our knowledge of the behavior of polluting trace elements is far from complete. The persistence of contaminants in soil is much longer than in other components of the biosphere, and contamination of soil, especially by heavy metals, appears to be virtually permanent. Metals accumulated in soils are depleted slowly by leaching, plant uptake, erosion, or deflation. The first half-life of heavy metals, as calculated by Iimura et al.[336] for soils in lysimetric conditions, varies greatly — for Zn, 70 to 510 years; for Cd, 13 to 1100 years; for Cu, 310 to 1500 years; and for Pb, 740 to 5900 years.

The input-output balance of metals in soils discussed in Chapter 3, Section III. B. shows that trace metals concentrations in surface soil are likely to increase, on a global scale, with growing industrial and agricultural activities. There are several indications that the composition of surface soil may be influenced by both local contamination and long-range transport of pollutants. Purves[634] concluded that the extent of soil contamination in the urban environment is now so great that it is possible to identify most soils as urban or rural on the basis of their content of a few trace metals that are known to be general urban contaminants. The annual increment of heavy metals caused by dust fallout in Tokyo is estimated for Cd to be 0.05 ppm and for Pb and Mn to be about 0.5 ppm.[395]

The regional contamination of soils, as reported most commonly, occurs mainly in industrial regions and within centers of large settlements where factories, motor vehicles, and municipal wastes are the most important sources of trace metals. However, due to the long distance aerial transport of trace pollutants, especially those which form volatile compounds (e.g., As, Se, Sb, and Hg), it has become difficult to estimate the natural background values for some trace elements in soils.

In addition to aerial sources of trace pollutants, fertilizers, pesticides, and all sewage-derived materials have added to the trace element pool in soils. The mobilization of heavy metals from smelter and mine spoil by transport with seepage waters or by windblown dust may also be an important source of soil contamination in some industrial regions. The variability of trace element concentrations in materials used in agriculture is presented in Table 5. Goodroad,[273] Piotrowska and Wiacek,[620] and Stenström and Vahter[755a] reported that long-term use of inorganic phosphate fertilizers adds substantially to the natural levels of Cd and F in soils, while other elements such as As, Cr, Pb, and V do not increase significantly. Effects of sewage sludge applications on soil composition are especially of great environmental concern and have been the subject of many studies and much legislation. Advisory standards and guidelines for safe addition of trace elements in sewage sludge to land is still in the stage of experiment and negotiation; however, several authors have given threshold values for the maximum addition of trace elements in one dose and over a period of time (Table 6). In spite of some diversity of opinion, there is general agreement, especially regarding the maximum concentrations of heavy metals in soils. Maximum allowable limits set up for paddy soils in Japan are somewhat different.[395] Cu content was established at 125 ppm (0.1 *N* HCl soluble) and As was established at 15 ppm (1 *N* HCl soluble) as critical for rice growth. The hazardous concentration in soils of Cd is limited by allowable Cd in rice, which should not exceed 1 ppm. It should be emphasized, however, that all the allowable limits need to be related not only to the given plant-soil system, but also to ratios between single elements as well as to their total burden in soil.

In several soils the threshold levels already have been exceeded either in gardens and

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TABLE VIII

TISSUE LEVELS OF Hg AFTER 7 WEEKS IN SPECIAL F3a GENERATION STUDY

Tissue	0 ppm	0 + 25 ppm	0.1 + 25 ppm
Blood (total Hg)	0.18 ± 0.034	146 ± 18.1	227 ± 21.5 xx
Kidneys (total Hg)	0.47 ± 0.15	86.8 ± 8.75	92.8 ± 17.5
Liver (MeHgCl)	—	67.9 ± 2.2	84.8 ± 6.5 xx
Brain (MeHgCl)	—	10.6 ± 0.9	12.9 ± 1.3 x

Tissue	0.5 + 25 ppm	2.5 + 25 ppm
Blood (total Hg)	227 ± 37.0 xx	151 ± 26.1
Kidneys (total Hg)	79.2 ± 13.1	81.3 ± 15.2
Liver (MeHgCl)	103 ± 24 xx	87.6 ± 3.6 xx
Brain (MeHgCl)	11.0 ± 1.3	11.2 ± 1.5

Values are for group of 5 males.
x, $P < 0.05$; xx, $P < 0.01$.
Significance is calculated compared with the 0 + 25 ppm group.

and the brain were significantly increased when compared with the 0 ppm control group (Table VII). The relative liver weight of females was increased non-significantly in all 25 ppm groups. When the individual groups were compared to the 0 + 25 ppm group, increased relative weights were seen in the kidneys and brain of females on 0.5 + 25 ppm and on 2.5 + 25 ppm and in the kidneys of males on 0.1 + 25 ppm and on 2.5 + 25 ppm.

The characteristic lesions of the nervous system and kidneys seen histologically in the short-term study were found in all groups which received 25 ppm. No differences between the treated groups could be observed. Lesions in the cerebellum were only observed in treated females. MeHgCl administration to the parent generation did not profoundly affect tissue concentrations in the F3a generation and except for blood the concentrations obtained at various dose levels were comparable (Table VIII).

DISCUSSION

For ease of comparison, the results obtained in the reproduction study have been discussed in the light of those obtained in the short- and long-term studies. The discussion appears in the report on the long-term study.

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